

Photoacoustic Spectroscopy for Quantitation of Trace Gases in Air

The instruments commonly used for the real-time field-based detection of air-borne chemical warfare agents (CWAs), toxic industrial compounds (TICs), and pollutants must be periodically calibrated and they often exhibit a nonlinear mixture-dependent response. Examples include ion mobility spectrometers, electro-chemical sensors, and colorimetric sensors. In practice the field-based detectors are not traceable to either gas concentration standard mixtures or to the SI. Consequently, the reliability of field measurements of CWAs and TICs cannot be adequately quantified, a circumstance that leads to false positive and/or false negative detection of chemical threats in the field. NIST's goal is to develop a stable, high-sensitivity instrument that quantifies the amounts of specific trace gases in air. This instrument will be used as a field-deployable transfer standard for trace gas detection technology with emphasis on CWAs, TICs, and air pollutants.

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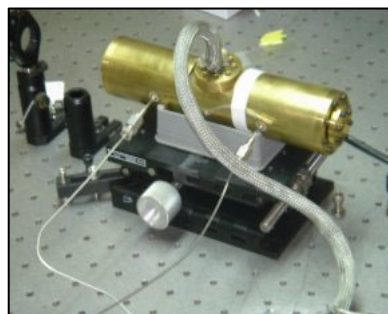
The current method for characterizing and calibrating field sensors requires the use of high-performance analytical instruments such as gas chromatographs (GC) and/or mass spectrometers (MS). However, GC/MS techniques typically require pre-concentration of the analyte and/or calibration against a known reference; these steps add significant uncertainty to the measurement. Other weaknesses of these protocols are: (1) they are expensive, (2) they do not operate in real time, and (3) they require a laboratory environment. To address this measurement need, NIST is developing photoacoustic spectroscopy for the routine field-based calibration of portable atmospheric analyzers.

This NIST research team combined expertise in acoustics and laser optics to develop a portable, robust, sensitive and species-specific spectroscopic method for analysis of trace quantities (nmol/mol levels) of CWA and TIC compounds in atmospheric samples. The new technique is called cavity-enhanced photoacoustic spectroscopy (CE-PAS); it combines the ruggedness and simplicity of photoacoustic spectroscopy (PAS) with the high sensitivity and high selectivity of cavity-enhanced laser absorption spectroscopy. The fundamental idea is that species-specific, reproducible, concentration measurements can be obtained by probing the infrared absorption spectrum of the target

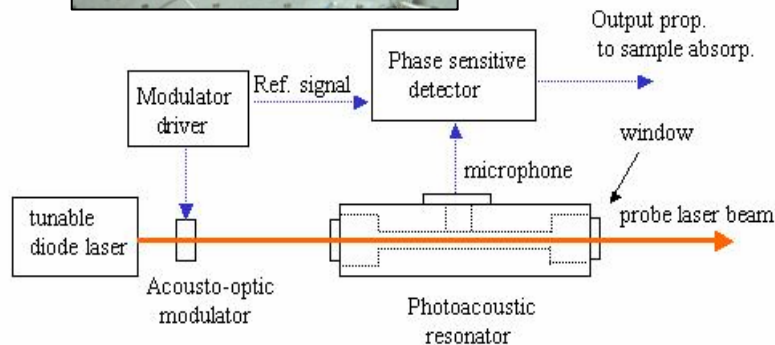
IDLH – Immediate Danger to Life & Health		
Substance	Type	IDLH level
Acrolein	TIC	2 $\mu\text{mol/mol}$
Hydrogen cyanide	CWA	50 $\mu\text{mol/mol}$
Mustard	CWA	0.4 nmol/mol
Nitrogen dioxide	TIC	20 $\mu\text{mol/mol}$
Phosgene	CWA	2 $\mu\text{mol/mol}$
Sarin	CWA	30 nmol/mol
Soman	CWA	8 nmol/mol
Sulfur dioxide	TIC	100 $\mu\text{mol/mol}$
Tetraethyl lead	TIC	3 $\mu\text{mol/mol}$

analyte(s). With the PAS method, the probe laser is tuned to a wavelength at which the analyte absorbs light. The light absorbed by the analyte creates a proportional change in the local pressure that propagates through the gas in the cell. When the laser's intensity is modulated at a frequency near an acoustic resonance, a steady-state acoustic wave is generated that can be detected using a microphone and a lock-in amplifier.

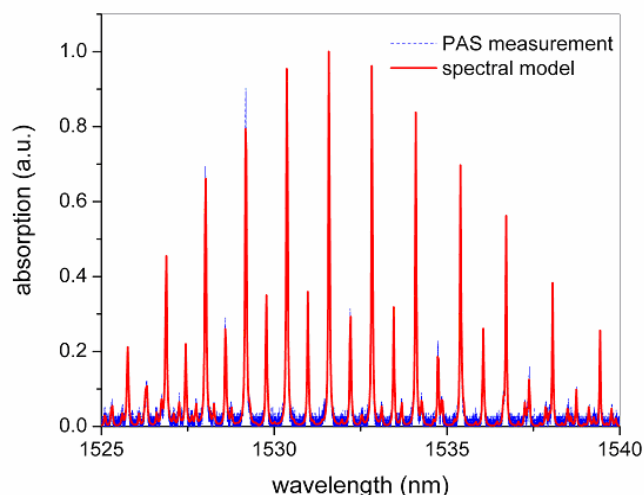
The acoustic signal is proportional to the analyte concentration, and the constant of proportionality is readily predicted from NIST-measured absorption cross-sections. The acoustic signal is proportional to the probe beam power; therefore, relatively high laser power is required to achieve low detection limits. Conventional photoacoustic detectors are either too large (using large, high-power CO₂ lasers) or are broadband with insufficient selectivity, sensitivity, or accuracy. We are using compact, tunable single-mode solid-state lasers because they are suitable for spectroscopic measurements in the near and mid-infrared spectral region. To achieve low detection limits with these solid-state lasers, we will amplify their modest output power by a factor of 100 by using a resonant optical cavity. Thus, the combination of optical and acoustic resonators will enable the realization of compact, field-deployable absorption spectrometers suitable as transfer standards for the measurement of absolute analyte concentration.



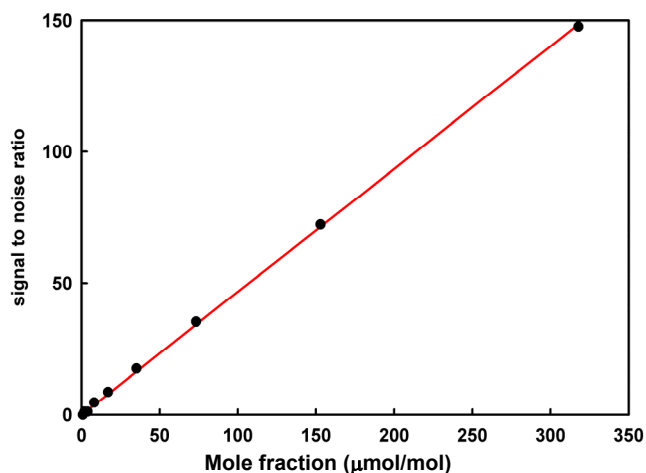
The NIST team began developing this instrument in 2005, and constructed the PAS system shown in the photograph and the schematic diagram.



This compact system includes an external cavity diode laser with 20 mW of output power and single-mode tunability over the range 1.52 μm to 1.55 μm , an acousto-optic modulation system for intensity modulation of the laser power, a custom acoustic resonator with a quality-factor $\cong 40$ and a low-noise MEMs-based microphone. We tested this system in ambient air with C_2H_2 as a surrogate analyte in concentrations from 10^{-6} mol/L to 0.004 mol/L. A gas mixing and sampling system was built to deliver fixed concentrations of the analyte. Rovibrational spectra of C_2H_2 in air were measured with a spectral resolution better than 10 MHz. The figure shows the absorption spectrum of C_2H_2 vibrational overtone band obtained with the photoacoustic spectrometer and external cavity diode laser system. The modeled spectrum is based on the HITRAN database for C_2H_2 .



This measurement yielded a PAS signal response linear in concentration with detection limits near 1 $\mu\text{mol/mol}$. The figure below shows the signal to noise ratio (S/N) and linear regression as a function of mole fraction for C_2H_2 in air measured with the PAS system shown in the figure above. S/N = 1 corresponds to about 1 $\mu\text{mol/mol}$.



Future Plans:

The NIST team plans to demonstrate practical CEPAS measurements of known samples of surrogates (when necessary) and relevant analytes. This will require the development of safe, accurate gas mixing and sampling systems for preparation of known mixtures, and the realization of a modular and portable CEPAS spectrometer. Critical issues include identification of limiting sources of noise (e.g., background effects from window absorption, electro-magnetic interference in the microphone, laser instabilities, flow turbulence, etc.) and optimization of the cavity-enhanced photoacoustic measurement technique. Matrix-dependent phenomena need to be investigated and quantified, including the effects of acoustic interactions, pressure broadening by air and water vapor, and spectral clutter from interfering gases such as hydrocarbon vapors. These investigations will yield spectroscopic properties of relevant compounds linked to the SI, and will provide the capability to render CEPAS as a viable transfer standard for measurements of CWAs, TICs, and pollutants. Ultimately, all components of the spectrometer shall be completely defined and specified so that a compact portable spectrometer can be engineered by a third party for system replication and dissemination. This will require ongoing consultation with instrument manufacturers, customers, and end-users.